BIODIESEL PRODUCTION VIA TWO-STEPS CATALYZED PROCESS: THE STUDY ON EFFECT OF TEMPERATURE AND CATALYST WEIGHT PERCE4NT TO THE BIODIESEL YIELD, FFA CONTENT AND ACID VALUE

AMMINATUL FARHAYU BINTI ABDUL TALIB

A report submitted in partial fulfillment of the requirements for the award of the degree of Bachelor of Technology (Chemical Engineering and Natural Resource)

Faculty of Chemical Engineering and Natural Resource
University Malaysia Pahang

MARCH 2008

‘I declare that this thesis is the result of my own research expect as cited references. The thesis has not been accepted for any degree and is concurrently submitted in candidature of any degree.”

Signature :………………………………………………………

Name of Candidate : AMMINATUL FARHAYU BINTI ABDUL TALIB

Date :

En route for beloved father, my late mother, family, friends and those people who'd giving me support and understanding and the help to finish my journey…

ACKNOWLEDGEMENT

In preparing this thesis, I was in contact with many people, researchers, academicians and practitioners. They have contributed a lot towards my understanding and thoughts. In particular, I wish to express my sincere appreciation to my main supervisor, Ms Shalyda Binti Md Shaarani@Md Nawi for encouragement, guidance, critics and friendship. I am also very thankful to my ex-supervisor Mdm Ruzinah Isha for her guidance, advice and also motivation. I am also indebted to FKKSA lectures for their guidance to complete this thesis. Without their continued support and interest, this thesis would not have been the same as presented here.

My sincere appreciation also extends to all my colleagues and other who have provided assistance at various occasions. Their views and tips are useful indeed. Unfortunately, it is not possible to list all of them in this limited space. I am grateful to all my members in UMP.

ABSTRACT

In this study, the effects of temperature and catalyst weight percent to the biodiesel yield, FFA content and acid value were studied. The biodiesel is produced by two-steps catalyzed process. The essential part of the process is the transesterification of waste cooking oil (WCO) with methanol in present of catalyst, to yield methyl ester as the main product and glycerin as the by-product. In the acid treatment or the acid-catalyzed esterification, the temperature is set at 95°C, acid catalyst of 2%w/wH_2SO_4 and methanol to waste cooking oil of 10:1. For the alkali-catalyzed transesterification, the range of temperature is 40°C-80°C, the alkali catalyst weight percent is varied from 0.2 to 1.0%wNaOH/wWCO. The ultrasonic wave and ratio of methanol to waste cooking was fixed at 32MHz and 6:1 respectively. The biodiesel product is then analyzed by titration to check the FFA content and the acid value. The best temperature and alkali catalyst weight percent was found at 70°C and 1.0%wNaOH/wWCO correspondingly. The total reduction of FFA content after acid treatment was 36.92%. The two steps catalyzed process is preferable for raw material that has high content of FFA such as waste cooking oil.

ABSTRAK

Dalam kajian ini, kesan suhu dan peratus berat mangkin terhadap mintak masak terpakai dikaji terhadap hasil, kandungan asid lemak bebas, dan juga nilai asid biodiesel telah dikaji. Biodiesel dihasilkan dengan menggunakan proses dua langkah bermangkin. Secara kasarnya, bahagian penting dalam proses ini adalah transesterifikasi minyak masak terpakai dengan methanol dengan kehadiran mangkin untuk menghasilkan biodiesel sebagai hasil utama dan glycerin sebagai hasil sampingan. Semasa process rawatan asid, suhu telah ditetapkan pada 95°C, mangkin asid 2%w/wH_2SO_4 dan methanol terhadap minyak masak terpakai 10:1. Untuk proses traneseterifikasi bermangkin alkali jarak suhu dipelbagaikan di antara 40°C-80°C, nisbah berat mangkin terhadap minyak masak di antara 0.2 to 1.0%wNaOH/wWCO. Gelombang ultrasonic dan nisbah methanol terhadap minyak masak masing-masing ditetapkan pada 32MHz dan 6:1. Biodiesel yang terhasil diuji dengan menggunakan kaedah pentitratan untuk menguji kandungan asid lemak bebas dan juga tahap kandungan asid. Suhu terbaik yang telah ditemui adalah pada 70°C dan nisbah berat mangkin pada 1.0%wNaOH/wWCO. Jumlah pengurangan asid lemak bebas selepas process rawatan asid adalah 36.92%. Proses dua langkah bermangkin ini lebih bermakna apabila menggunakan bahan asas yang mempunyai kandungan asid lemak bebas yang tinggi seperti minyak masak terpakai.

TABLE OF CONTENT

LIST OF TABLE

LIST OF FIGURES

LIST OF APPENDICES

LIST OF SYMBOLS

Symbol	**Title**
P	Pressure
m	Mass
T	Temperature
°C	Degree Celsius
Pa	Pascal
Hz	Hertz
L	Liter
g	Gram
mg	Milligram
m	Meter
cm	Centimeter
%wt	Weight Percent

CHAPTER I

INTRODUCTION

Worldwide economies are struggling to cope with the raising crude oil prices and at the same time need to negotiate with the environmental concern associated with fossil fuel usage. Therefore, countries across the world are now penetrating viable alternative to fossil fuels that are cost-effective and environmental friendly. As the result, biofuels are gaining popularity, especially in transport sectors, across the globe. Consumption of biofuels is aimed to minimize over-dependence of conventional and expensive fossil fuel. Apart from reducing pollution, biofuels usage offers economies benefits such as increased job opportunities, and contributes in strengthening the agriculture sector.

Biodiesel and bioethanol are the primary biofuels currently in used across the world. The demand of biodiesel is rapidly increasing even though bioethanol is them most widely consumed. Rising the environmental pollution and volatile prices of petroleum diesel are supercritical factors that increased the demand for the biodiesel worldwide.

1.1 Biodiesel

Biodiesel is one of the alternative fuels having many advantages. It is derived from the renewable, domestic resource that relieves the reliance on petroleum fuel import. Biodiesel is biodegradable and non-toxic that made it safe to the environment. Compared to the petroleum based diesel, biodiesel have more favorable combustion emission profile, such as low emission of carbon monoxide produced by particulate matter and unburned hydrocarbons. Carbon dioxide produced by combustion of biodiesel can be recycled by photosynthesis and reducing the impact of biodiesel combustion on the greenhouse effect. Biodiesel is light to dark yellow liquid, practically immiscible with water, has a high boiling point and low vapor pressure. High flash point which is 150°C makes it less volatile and safer. In brief, these merits of biodiesel make it a good alternative to petroleum-based fuel and have led to its use in many countries, especially in environmentally sensitive areas.

1.2 Transesterification

The transesterification process is the reaction of triglyceride (fat/oil) with alcohol to form esters and glycerol. During the esterification process, the triglyceride is reacted with alcohol in the presence of a catalyst; usually strong base liked potassium hydroxide. The alcohol reacts with fatty acids to form the mono-alkyl ester, or biodiesel and crude glycerol. In most production methanol or ethanol is the alcohol used (methanol produces methyl esters, ethanol produces ethyl esters) and is alkali-catalyzed by either potassium or sodium hydroxide. Potassium hydroxide has been found to be more suitable for the ethyl ester biodiesel production; either alkali can be used for the methyl ester. A common product of the transesterification process Rape Methyl Ester (RME) produced from raw rapeseed oil with methanol

Figure 1.1 shows the chemical process for methyl ester biodiesel. The reaction between the fat or oil and the alcohol is reversible reaction and so the alcohol must be added in excess to drive the reaction toward the right and ensure complete conversion.

$$\begin{array}{llllllll} CH_2\text{-}OOC\text{-}R_1 & & & & R_1\text{-}COO\text{-}R' & & CH_2\text{-}OH & \\ CH_2\text{-}OOC\text{-}R_2 & + & 3R'OH & \xleftrightarrow{\text{catalyst}} & R_2\text{-}COO\text{-}R' & + & CH\text{-}OH & (1.1) \\ CH_2\text{-}OOC\text{-}R_3 & & & & R_3\text{-}COO\text{-}R' & & CH_2\text{-}OH & \\ \textbf{Glyceride} & & \textbf{Alcohol} & & \textbf{Ester} & & \textbf{Glycerol} & \end{array}$$

Figure 1.1: Chemical reaction general equation for methyl ester biodiesel production

The products of the reaction are the biodiesel itself and glycerol. A successful transesterification is signified by the separation of the ester and glycerol layers after the reaction time. The heavy co-product, glycerol settles out and may be sold as it is may be purified for use in other industries (Gerpen, 2005).

1.3 Ultrasonic Transesterification

The latest technology used by many researchers to produce biodiesel is ultrasound technology or ultrasonic transesterification (Ji *et al*, 2006). Ultrasonic was proven to be an efficient method for the preparation of biodiesel by transesterification from oil. This method gives the shorter reaction time and less energy consumption than the conventional mechanical stirring method. It can produce almost 99% of biodiesel yield from oil. Ultrasound reduces the processing time from the conventional 1-5 hours processing batch to less than 5 minutes (Ji *et al*, 2006). It can also help to reduce the separation time from 10 to 5 hours. Moreover, the international standards for biodiesel ensures that important factors such as complete reaction, the removal of catalyst, the removal of alcohol, the absence of Free Fatty Acids (FFAs) and low sulfur content are adhere to.

1.4 Alkali-catalyzed Transesterification

Alkali-catalyzed transesterification process is more efficient and is less corrosive than acid-catalyzed process which makes it more applicable to industrial use. Alkali catalysts for transesterification process include metal hydroxides like sodium or potassium hydroxide, carbonates, and metal alkoxides. Increasing the concentration of catalyst in the mixture accelerate the reaction. The condition of activity of this catalyst is under anhydrous condition. However, this cannot be avoided as water is formed during the reaction between hydroxides and alcohols. The yield of alkyl esters is reduced as water hydrolyses the ester, forming soap. Soap forms an emulsion with glycerol making recovery of glycerol difficult (Zhang *et al*, 2002). This commonly catalyst used is sodium hydroxide due to its economical availability.

1.5 Acid-catalyzed Esterification (Pre-treatment Step)

When waste cooking oil (WCO) with more than 10%FFA is used, an acid catalyzed is preferred, but it requires more excess methanol, high pressure and high cost stainless steel equipment (Yong *et al*, 2002). In addition, the yield of product is low when the common sulfuric acid is used. Hence, a combine process with acid-catalyzed pre-treatment is developed to synthesize biodiesel from waste cooking oil. The first step would be the esterification of FFA with methanol by acid catalyst (sulfuric acid). The sulfuric acid is then drained before the homogenous alkali is introduced into the system to complete the transesterification.

To improve the acid catalyst pre-treatment process, the homogenous Lewis acid catalyst is used to synthesize biodiesel from waste cooking oil. However, the temperature used is quite high but the conversion is relatively low. So, the two steps catalyzed are adopted for the production of biodiesel. At the first step, sulfuric acid is introduced to catalyze the esterification reaction in which the FFAs in waste cooking oil reacted with methanol. The sulfuric acid is insoluble in the oil is centrifuge from the liquid after the methanol recovery and could be reused. At the second step, sodium hydroxide is added to catalyze the transesterification reaction in which Triglyceride (TG) reacted with methanol. Without waste water, reusing the catalyst and low cost reaction tank, these two steps shows the potential application in the biodiesel fuel industry.

1.6 Research Background and Problem Statement

Biodiesel is renewable fuel that can be used to power up the conventional diesel engines with little or no modifications. Biodiesel is composed of mono-alkyl esters of fatty acid chain from animal fat or vegetable oils. Waste vegetable oil will reduce the cost of biodiesel production, and will give the world a way to reuse the total production cost of biodiesel results from the cost raw material (Krawczyk, 1996). This cost is significantly lowered when waste cooking oil is used.

Waste cooking oil presents additional problems compared to virgin oil. These problems will be identified, and reactor configuration will be chosen that will minimize the cost of the reactor. The most obvious problem associated with WCO is that WCO may contain dirt, charred food and other material that would otherwise be present in vegetable oil. These materials should be filtered out of the oil before it enters the reactor.

The most common method of biodiesel production is the transesterification of the oils. Transesterification is affected by the molar ratio of alcohol to triglycerides, the catalyst used, the reaction temperature, reaction time and the FFAs and water content of the oil used. There are three main catalysts that are frequently used to produce biodiesel, alkali-catalyzed, acid-catalyzed or enzyme-catalyzed. However, for some circumstances, when the FFAs contain in the oil is relatively high, two-steps transesterification is needed. Therefore, the two-step catalyzed transesterification will be studied. The catalyst must be chosen first, because this affects the reaction temperature, time and the molar ratio of alcohol to WCO needed to complete the reaction.

1.7 Objective of the Research

The main objective of this study is to identify the effect of temperature and catalyst ratio to WCO to the yield, FFA content and the acid value of biodiesel, by two-steps catalyzed transesterification assisted by ultrasonic radiation.

1.8 Scope of the Research

To achieve all the objective stated above, the scope of the study is identified and listed as below;

- Raw material preparation
- Acid catalyst preparation
- Acid-catalyzed transesterification
- Alkali catalyst preparation
- Alkali-catalyzed transesterification
- Product purification
- Product analysis

In the raw material preparation step, WCO is first need to be filtered to remove the dirt and small particles might contain in WCO. The WCO is now ready to go through the first step acid-catalyzed transesterification. After the acid catalyst preparation, now the reaction can be run. After reaction is complete, the alkali catalyst is prepared so that the second step of the experiment which is the alkali-catalyzed transesterification can be started. The product is then let to settle for one night before can be purify and going through the analysis.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Diesel-petroleum based has released problems such as toxicity, water, land and air pollution, fire risk, non-biodegradability and limited resources had opened a unique opportunity to produced new environmental acceptable fuel and lubricants derived from natural ester like vegetable oil. Reported that, the world production of 17 major oils and fats are over 100 billion tones and out this 79% are from vegetable oil (Hamm and Hamilton, 2002).

Research, development and application of vegetable based oil in industrial and automotive sectors are rapidly increasing. The attractive part of vegetable oil is they are neutral, non-toxic, biodegradable, and relatively non-polluting and derived from renewable raw material. During the last decade, due to strict government and environment regulation almost of all country in the world, there has been constant demand for environmentally friendly fuel (Rhee, 1996). Most of fuel originates from petroleum stock which is toxic to environment and difficult to dispose. Vegetable oils with high oleic acid content are considered to be potential candidates to substitute conventional mineral oil base fuel oils and synthetic esters.

Although biodiesel cannot entirely replace petroleum-based diesel fuel, there are at least five reasons that justify its development (Gerpen, 2005):

I. It provides a sufficient market for excess production of vegetable oils and fats.

II. It decreased, although will not eliminate, most country's dependencies on imported petroleum.

III. Biodiesel is renewable and does not contribute to global warming due to its closed carbon cycle. A life cycle analysis of biodiesel showed that generally CO_2 emissions were reduced by 78% compared with petroleum-based diesel fuel (Shehan *et al*, 1998).

IV. The exhausts emissions of carbon monoxide, unburned hydrocarbons, and particulate emissions from biodiesel are lower that with regular diesel fuel. Unfortunately, most emissions test has shown a slight increased of nitrogen oxides (NO_x).

V. When added to regular diesel fuel in an amount equal to 1-2%, it can convert fuel with poor lubricating properties, such as modern ultra-low-sulfur diesel fuel, into an acceptable fuel.

In 1997, the production of biodiesel fuel was 550,000 tones in Europe, 10,000 tones in Malaysia and 9000 tones in North America. In 2000, the annual production of biodiesel in Europe was 1,210,000 tones. The production increased 2.2 times in three years (Kann *et al*, 2002).

2.2 Characteristic of Biodiesel

Biodiesel is well known as an alternative fuel for diesel engines that is chemically produced by reacting the virgin or used vegetable oil or animal fats with an alcohol such as methanol in order to accelerate the reaction (Leung *et al*, 2006).

Figure 2.1 shows an example of biodiesel. However, it colors cab be varied between golden and dark brown because it depends on the production feedstock. It is practically immiscible with water, has high boiling point and low vapor pressure. Typical methyl ester biodiesel has a flash point of ~150°C (300°F), making it rather non-flammable. Biodiesel has density of ~0.88g/cm^3, less than water. Biodiesel that unpolluted with starting material can be regarded as non-toxic. It also has similar viscosity with petro-diesel that produces from petroleum.

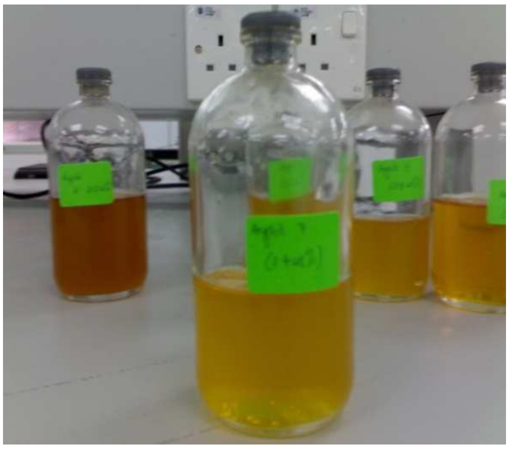

Figure 2.1: Example of biodiesel

Moreover, biodiesel is also clean burning diesel fuel replacement made from natural, renewable source, such as new and used vegetable oils or animal fats. It will run in any diesel engine with a little or no modification and can be mixed with regular diesel fuel in any ratio. Biodiesel is non-toxic and biodegradable.